

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

INVENTOR(S) Hubert MEIXNER et al

SERIAL NO: New Application

FILING DATE: Herewith

FOR: THE USE OF CROSSLINKED NITROGENOUS COMPOUNDS WHICH ARE SOLUBLE OR DISPERSIBLE IN WATER IN DETERGENTS AND CLEANERS

jc882 U.S. PTO
09/676780
10/02/00

FEE TRANSMITTAL

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

FOR	NUMBER FILED	NUMBER EXTRA	RATE	CALCULATIONS
TOTAL CLAIMS	6 - 20 =	0	× \$18 =	\$0.00
INDEPENDENT CLAIMS	1 - 3 =	0	× \$78 =	\$0.00
<input type="checkbox"/> MULTIPLE DEPENDENT CLAIMS (If applicable)			+ \$260 =	\$0.00
<input type="checkbox"/> LATE FILING OF DECLARATION			+ \$130 =	\$0.00
BASIC FEE				\$710.00
TOTAL OF ABOVE CALCULATIONS				\$710.00
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<input type="checkbox"/> FILING IN NON-ENGLISH LANGUAGE			+ \$130 =	\$0.00
<input type="checkbox"/> RECORDATION OF ASSIGNMENT			+ \$40 =	\$0.00
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09/676780

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Respectfully Submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.Norman F. Oblon
Registration No. 24,618John K. Pike, Ph.D.
Registration No. 41,253Date: 10/2/00**22850**Tel. (703) 413-3000
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(OSMMN 11/98)



10/02/00

09/676780
10/20/00
U.S. PTO

UTILITY PATENT APPLICATION TRANSMITTAL <small>(Only for new nonprovisional applications under 37 CFR 1.53(b))</small>	Attorney Docket No.	198049US0DIV
	First Inventor or Application Identifier	Hubert MEIXNER
	Title	THE USE OF CROSSLINKED NITROGENOUS COMPOUNDS WHICH ARE SOLUBLE OR DISPERSIBLE IN WATER IN DETERGENTS AND CLEANERS

APPLICATION ELEMENTS <small>See MPEP chapter 600 concerning utility patent application contents</small>	ADDRESS TO: Assistant Commissioner for Patents Box Patent Application Washington, DC 20231
<p>1. <input checked="" type="checkbox"/> Fee Transmittal Form (e.g. PTO/SB/17) (Submit an original and a duplicate for fee processing)</p> <p>2. <input checked="" type="checkbox"/> Specification Total Pages 50</p> <p>3. <input type="checkbox"/> Drawing(s) (35 U.S.C. 113) Total Sheets </p> <p>4. <input checked="" type="checkbox"/> Oath or Declaration Total Pages 4</p> <p>a. <input type="checkbox"/> Newly executed (original or copy)</p> <p>b. <input checked="" type="checkbox"/> Copy from a prior application (37 C.F.R. §1.63(d)) (for continuation/divisional with box 15 completed)</p> <p>i. <input type="checkbox"/> DELETION OF INVENTOR(S) Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §1.63(d)(2) and 1.33(b).</p> <p>5. <input checked="" type="checkbox"/> Incorporation By Reference (usable if box 4B is checked) The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4B, is considered to be part of the disclosure of the accompanying application and is hereby incorporated by reference therein.</p>	ACCOMPANYING APPLICATION PARTS <p>6. <input type="checkbox"/> Assignment Papers (cover sheet & document(s))</p> <p>7. <input type="checkbox"/> 37 C.F.R. §3.73(b) Statement (when there is an assignee) <input type="checkbox"/> Power of Attorney</p> <p>8. <input type="checkbox"/> English Translation Document (if applicable)</p> <p>9. <input checked="" type="checkbox"/> Information Disclosure Statement (IDS)/PTO-1449 <input checked="" type="checkbox"/> Copies of IDS Citations</p> <p>10. <input checked="" type="checkbox"/> Preliminary Amendment</p> <p>11. <input checked="" type="checkbox"/> White Advance Serial No. Postcard</p> <p>12. <input type="checkbox"/> Small Entity Statement(s) <input type="checkbox"/> Statement filed in prior application. Status still proper and desired.</p> <p>13. <input type="checkbox"/> Certified Copy of Priority Document(s) (if foreign priority is claimed)</p> <p>14. <input checked="" type="checkbox"/> Other: Request for Priority Translation of Category of Cited Documents in Attached International Search Report Copy of Form PCT/DO/EO/903 International Search Report English Translation of the Annexes to the International Preliminary Examination Report (Pages 46-49)</p>
<p>15. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below:</p> <p><input type="checkbox"/> Continuation <input checked="" type="checkbox"/> Divisional <input type="checkbox"/> Continuation-in-part (CIP) of prior application no.: 09/500,534</p> <p>Prior application information: Examiner: John R. Hardee Group Art Unit: 1751</p>	
<p>16. Amend the specification by inserting before the first line the sentence:</p> <p><input checked="" type="checkbox"/> This application is a <input type="checkbox"/> Continuation <input checked="" type="checkbox"/> Division <input type="checkbox"/> Continuation-in-part (CIP) of application Serial No. 09/500,534, filed on February 9, 2000, pending, which is a divisional application of 09/284,456, filed May 12, 1999, (now U.S. Patent No. 6,083,898, Issued on July 4, 2000), which was originally filed as International Application No. PCT/EP97/05744, filed October 17, 1997.</p> <p><input type="checkbox"/> This application claims priority of provisional application Serial No. Filed </p>	
17. CORRESPONDENCE ADDRESS 22850 (703) 413-3000 FACSIMILE: (703) 413-2220	

Name:	Norman F. Oblon	Registration No.:	24,618
Signature:		Date:	10/2/00
Name:	John K. Pike, Ph.D.	Registration No.:	41,253

Docket No. 198049US0DIV

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

INVENTOR(S) Hubert MEIXNER et al

SERIAL NO: New Application

FILING DATE: Herewith

FOR: THE USE OF CROSSLINKED NITROGENOUS COMPOUNDS WHICH ARE SOLUBLE OR DISPERSIBLE IN WATER IN DETERGENTS AND CLEANERS

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Respectfully Submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.

Norman F. Oblon
Registration No. 24,618

John K. Pike, Ph.D.
Registration No. 41,253

Date: 10/2/00



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(OSMMN 11/98)

I:\atty\JKP\198049.fee.wpd

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: :

Hubert MEIXNER et al :

SERIAL NO.: New U.S. Application :

FILED: Herewith :

FOR: THE USE OF CROSSLINKED
NITROGENOUS COMPOUNDS WHICH
ARE SOLUBLE OR DISPERSIBLE IN
WATER IN DETERGENTS AND CLEANERS

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

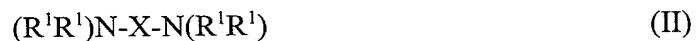
Prior to examination on the merits, please amend the above-identified application.

IN THE CLAIMS

Please cancel Claims 1-7.

Please amend the following claims as indicated (all pending claims are reproduced for the Examiner's convenience):

--8. (Amended) A water-soluble crosslinked product obtainable by crosslinking amines of the formula (II)



where the radicals R^1 are $(R^2R^2)N-(CH_2)_n$ radicals,

the radicals R^2 are hydrogen atoms or $(R^3R^3)N-(CH_2)_n$ - radicals,

the radicals R^3 are hydrogen atoms or $(R^4R^4)N-(CH_2)_n$ - radicals,

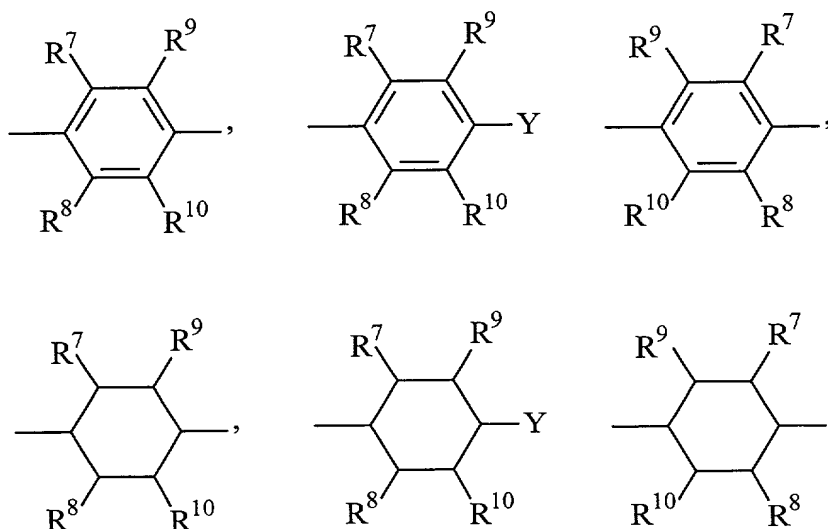
the radicals R^4 are hydrogen atoms or $(R^5R^5)N-(CH_2)_n$ - radicals,

the radicals R^5 are hydrogen atoms or $(R^6R^6)N-(CH_2)_n$ - radicals,

the radicals R^6 are hydrogen atoms,

n is 2, 3 or 4, and

the radical X is one of the radicals



$-(CH_2)_p$ -, $-(CH_2)_3-NR^{11}-(CH_2)_3$ -, $-(CH_2)_1-\{O-(CH_2)_k\}_m-O-(CH_2)_1-C_{2-20}$ -alkylene,

the radical Y is an oxygen atom, a $CR^7R^9C=O$ or SO_2 radical,

p is an integer from 2-20,

l and k are, independently of one another, an integer from 2-6, m is an integer from 1-40,

the radicals R^7 , R^8 , R^9 and R^{10} are, independently of one another, hydrogen atoms or C_{1-6} -alkyl radicals,

and the radical R^{11} is C_{1-20} -alkyl, C_{2-20} -dialkylamino- C_{2-10} -alkyl, C_{1-10} -alkoxy- C_{2-10} -alkyl, C_{2-20} -

hydroxyalkyl, C₃₋₁₂-cycloalkyl, C₄₋₂₀-cycloalkylalkyl, C₂₋₂₀-alkenyl, C₄₋₃₀-dialkylaminoalkenyl, C₃₋₃₀-alkoxyalkenyl, C₃₋₂₀-hydroxyalkenyl, C₅₋₂₀-cycloalkylalkenyl, an aryl or a C₇₋₂₀-arylalkyl radical which is unsubstituted or substituted one to five times by C₁₋₈-alkyl, C₂₋₈-dialkylamino, C₁₋₈-alkoxy, hydroxyl, C₃₋₈-cycloalkyl and/or C₄₋₁₂-cycloalkylalkyl, or two radicals R¹¹ together form an alkylene chain which may be interrupted by nitrogen or oxygen, such as from ethylene oxide, propylene oxide, butylene oxide and -CH₂-CH(CH₃)-O- or polyisobutylene with 1 to 100 isobutylene units,

with at least one bifunctional crosslinker (b) [as defined in claim 1] which reacts with NH groups.

9. A water-soluble crosslinked product of claim 8, in which the amine of general formula (II) is N,N,N',N'-tetraaminopropyl-1,2-ethylene diamine.--

Please add the following new claims:

--10. The product as claimed in Claim 8, wherein the crosslinker (b) is selected from the group consisting of the halogen-free crosslinkers:

- (1) polyepoxides,
- (2) ethylene carbonate, propylene carbonate and/or urea,
- (3) monoethylenically unsaturated carboxylic acids and their esters, amides and anhydrides, at least dibasic carboxylic acids or polycarboxylic acids, and their esters, amides and anhydrides,
- (4) products of the reaction of polyetherdiamines, alkylenediamines, polyalkylenepolyamines, bifunctional or multifunctional alcohols, alkylene glycols, polyalkylene glycols, functionalized polyesters or polyamides or their mixtures with monoethylenically unsaturated carboxylic acids or their esters, amides or anhydrides, the reaction products having at least two ethylenic double bonds, carboxamide, carboxyl or ester

groups as functional groups,

(5) products, containing at least two aziridino groups, of the reaction of dicarboxylic esters with ethyleneimine,

(6) cumulenes and polyheterocumulenes,

(7) β -keto esters, β -keto acids and β -keto aldehydes,

(8) functionalized glycidyl ethers;

the halogen-containing crosslinkers:

(9) polyhalides,

(10) glycidyl halides,

(11) chloroformates and chloroacetic acid derivatives,

(12) epichlorohydrin, glycerol chlorohydrin, polyether dichlorohydrin compounds,

(13) phosgene;

and mixtures thereof.

11. The product as claimed in Claim 8, wherein the crosslinker (b) is a bisglycidyl ether of a polyethylene glycol with a weight average molecular weight of from 300 to 3000.

12. A detergent or cleaner comprising the product as defined in Claim 8, and at least one surfactant.

13. The detergent or cleaner as claimed in Claim 12, further comprising at least one enzyme.--

REMARKS

Claims 1-7 have been canceled. Claim 8 has been amended to incorporate the crosslinker limitations of Claim 1, from which it formerly depended. Support is found in Claims 1 and 8 as originally filed.

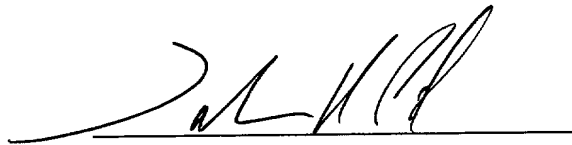
New Claims 10-13 have been added and find support in Claims 3, 4, 6 and 7 as originally filed.

No new matter is believed to be added to the application by entry of the amendments. Upon entry of the amendments, Claims 8-13 will be active. Entry and favorable consideration are respectfully requested.

Applicants respectfully submit that this application is now in condition for examination on the merits, and early notice of such action is earnestly solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
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**The use of crosslinked nitrogenous compounds which are soluble or dispersible in
water in detergents and cleaners**

The invention relates to the use of crosslinked nitrogenous compounds which are
soluble or dispersible in water in detergents and cleaners. The invention particularly
relates to the use of crosslinked oligo- and polyamines as soil release agents and
enzyme stabilizers in detergents and cleaners

The use of nitrogenous polymers in detergents is known

DE-A1-31 24 210 describes liquid detergents with additives to prevent dye transfer.
The detergent additionally contains nonionic or zwitterionic surfactants in combination
with polyethyleneimines, polyamines, polyamineamides or polyacrylamides, by which
transfer of dyes from colored textiles to white or pale-colored textiles on washing
together is counteracted. The polyamineamides can be obtained by condensing
polybasic acids such as dibasic, saturated, aliphatic C₃₋₈-acids and polyamines. The
polymers are described as soluble in water but are not identified more exactly.

DE-A-1 922 450 describes detergents and cleaners which contain antiredeposition
agents to prevent reabsorption of detached soil on the cleaned surfaces. Polyamides
which can be prepared from polyethyleneimines with an average molecular weight of
from 300 to 6000 and di- and tricarboxylic acids are used as antiredeposition agents.
Products of reactions with diglycolic acid, thiodiglycolic acid, iminodiacetic acid and
nitrilotriacetic acid are also mentioned.

DE-A-2 165 900 describes detergents with a content of antiredeposition additives. The
product of the reaction of a polyethyleneimine with a molecular weight of from 430 to
10,000 with C₈₋₁₈-alkyl glycidyl ethers, which may additionally be reacted with ethylene
oxide, is used as antiredeposition agent

It is furthermore known to use soil release agents, which are reversibly adsorbed from the wash liquor on the textile or the fibers of the textile during the washing process, in detergents. When a textile treated with such a soil release agent is soiled, in the next wash the adsorbed soil release agent improves detachment of the soil. This soil release effect is thus a reversible antisoil finish on the textile during the washing. Various soil release agents are known, such as polyesters from polyethylene oxides with ethylene glycol and/or propylene glycol and aromatic and/or aliphatic dicarboxylic acids. For example, DE-A-43 44 357 describes a soil release polymer which has ethylene glycol terephthalic groups and polyethylene glycol terephthalic groups.

10

In addition, modified celluloses, such as methylcellulose, hydroxypropylcellulose or carboxymethylcellulose, have been employed. US 4,138,352 describes the combination of a nonionic surfactant and a hydroxybutylated methylcellulose with low molecular weight as soil release agent.

15

EP-A1-0 042 187 describes detergent compositions which contain small amounts of substituted polyamines. The polyamines are in this case substituted by a long-chain alkyl or alkenyl radical. They may additionally be substituted by at least two alkylene oxide residues on different nitrogen atoms. The compositions show in particular improved soil release properties.

20

It is an object of the present invention to provide soil release agents for detergents and cleaners which preferably also act as enzyme stabilizers and have an advantageous property profile.

25

We have found that this object is achieved by the use of crosslinked nitrogenous compounds which are soluble or dispersible in water and are obtainable by crosslinking of

30

- (a) compounds containing at least three NH groups with
- (b) at least bifunctional crosslinkers which react with NH groups,

in detergents and cleaners.

The NH groups can be present in primary (NH₂) and/or secondary (NH) amino groups.

The nitrogenous compounds according to the invention are preferably used as soil release agents and/or enzyme stabilizers.

5

The soil release effect presumably derives from the adsorption, described above, of the agent from the wash liquor onto the textile. The soil release effect thus emerges on washing several times. It must be distinguished from the single wash cycle or soil removal effect. The soil removal effect relates to detachment of soil directly on the first wash of a stained, non-pretreated fabric. Polyamines ethoxylated with ethylene oxide often show a single wash cycle or soil removal effect. It has been found, surprisingly, that oligo- and polyamines crosslinked in particular by polyether chains show soil release properties. The additional enzyme-stabilizing effect was unexpected because the stabilizing additives employed to date have been mainly boric acid derivatives with polyols and alkyl- or arylboronic acids.

15

The compounds employed according to the invention moreover show the advantageous properties in a large number of detergent formulations, such as heavy duty detergents, colored textile detergents, which can be in liquid or solid form.

20

Compounds (a)

The crosslinked nitrogenous compounds used according to the invention can be obtained by crosslinking of (a) compounds containing at least three NH groups.

25

Compounds (a) are preferably selected from oligo- and polyamines, polyalkylenepolyamines, polyamidoamines, polyamidoamines grafted with (poly)ethyleneimine, and mixtures thereof. Polyalkylenepolyamines are suitable as component (a). Polyalkylenepolyamines mean in the present connection compounds which contain at least three NH groups, eg. diethylene triamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, diaminopropylethylenediamine, trisaminopropylamine and polyethyleneimines. The polyethyleneimines preferably have an average molecular weight (M_w) of at least 300. The average molecular weight of the polyethyleneimines may be up to 1,000,000. Of particular interest industrially is the use

30

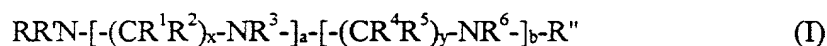
of polyethyleneimines with average molecular weights of from 600 to 25,000.

Also preferred are polyethyleneimine homopolymers with a degree of polymerization n of 5, 6, 10, 20, 35 and 100. These polyethyleneiminehomopolymers may be prepared either water-containing or anhydrous, or be dehydrated. Synthesis of appropriate polyethyleneimines is described in the examples.

The polyethyleneimines may also be partly modified, for example in one embodiment of the invention rendered hydrophobic with benzoic acid.

10

In one embodiment of the invention, the polyalkylenepolyamine is selected from amines of the formula (I)



15

where the radicals R, R' and R'', R¹, R², R⁴ and R⁵ are, independently of one another, hydrogen atoms, linear or branched-chain C₁₋₂₀-alkyl, -alkoxy, -hydroxyalkyl, -(alkyl)-carboxyl, -alkylamino radicals, C₂₋₂₀-alkenyl radicals or C₆₋₂₀-aryl, -aryloxy, -hydroxyaryl, -arylcarboxyl or -arylamino radicals, which may be further substituted, the radicals R³ and R⁶ are, independently of one another, hydrogen atoms, linear or branched-chain C₁₋₂₀-alkyl radicals, C₆₋₂₀-aryl radicals, which are unsubstituted or substituted, or radicals [(CR⁷R⁸)_z-NR⁹]-R¹⁰, where the radicals R⁷, R⁸, R⁹ and R¹⁰ are defined, independently of one another, as above for R, R', R'', R¹, R², R⁴, R⁵, or are carboxymethyl, carboxyethyl, phosphonomethyl or carbamoylethyl radicals, x, y and z are, independently of one another, 2, 3 or 4, and a, b and c are, independently of one another, integers from 0 - 300. there being at least three NH groups in the molecule.

25

5 to 100%, in particular 10 to 95%, of the nitrogen atoms in the above amines are preferably present in primary or secondary amino groups.

30

In one embodiment of the invention, the above amines have a number average molecular weight of from 80 to 150,000, preferably 100 to 50,000, particularly preferably 110 to 10,000, especially 129 to 5000.

The amine or polyalkylenepolyamine of the formula (I) may be a block copolymer or, in one embodiment of the invention, a polymer with randomly distributed blocks or a polymer with an overall random distribution.

5 Further suitable compounds (a) are polyamidoamines. They are obtained, for example, by reacting dicarboxylic acids having 4 to 10 carbon atoms with polyalkylenepolyamines preferably containing 3 to 20 basic nitrogen atoms in the molecule. The reaction products should have at least three NH groups. Examples of suitable dicarboxylic acids are succinic acid, maleic acid, adipic acid, glutaric acid, 10 suberic acid, sebacic acid or terephthalic acid. Mixtures of carboxylic acids can also be employed, eg. mixtures of adipic acid and glutaric acid or maleic acid and adipic acid or technical dicarboxylic acid mixtures such as Sokolan® DCS from BASF AG. Adipic acid or Sokolan® DCS is preferably used to prepare the polyamidoamines. Suitable polyalkylenepolyamines condensed with the dicarboxylic acids have been mentioned 15 above, eg. diethylenetriamine, triethylenetetramine, dipropylenetriamine, tripropylenetetramine, dihexamethylenetriamine, aminopropylethylenediamine and bisaminopropylethylenediamine. The polyalkylenepolyamines can also be employed in the form of mixtures for preparing the polyamidoamines. The polyamidoamines are preferably prepared without diluent, but this can also take place in inert solvents where 20 appropriate. The dicarboxylic acids are condensed with the polyalkylenepolyamines at elevated temperatures, eg. in the range from 100 to 220°C. The water formed in the reaction is distilled out of the reaction mixture. The condensation can, where appropriate, also be carried out in the presence of lactones or lactams of carboxylic acids having 4 to 8 carbon atoms. From 0.8 to 1.4 mol of a polyalkylenepolyamine are 25 normally used per mole of dicarboxylic acid. The polyamidoamines obtainable in this way have primary and secondary amino groups, contain tertiary nitrogen atoms and are soluble in water.

Also suitable as component (a) are polyamidoamines grafted with ethyleneimine. 30 Products of this type can be prepared by allowing ethyleneimine to act on the polyamidoamines described above in the presence of acids or Lewis acids, eg. sulfuric acid, phosphoric acid or boron trifluoride etherate. Ethyleneimine is grafted onto the polyamidoamine under the conditions described. It is possible, for example, to graft

from 1 to 20 ethyleneimine units on for each basic nitrogen group in the polyamidoamine, ie. about 10-1000, preferably 3-500, parts by weight of ethyleneimine are employed per 100 parts by weight of a polyamidoamine.

5 The polyalkylenepolyamines described above may be partially amidated. Products of this type are prepared, for example, by reacting polyalkylenepolyamines with mono-carboxylic acids or esters of monobasic carboxylic acids and monohydric C₁-C₄-alcohols. The polyalkylenepolyamines are preferably 1-30, usually only up to 20%,
10 amidated for the subsequent reactions. The amidated polyalkylenepolyamines must still have at least three free NH groups so that they can be reacted with the crosslinkers (b). Monocarboxylic acids having 1 to 28 carbon atoms can be employed for amidating the polyalkylenepolyamines for example. Examples of suitable carboxylic acids are formic acid, acetic acid, propionic acid, benzoic acid, salicylic acid, lauric acid, palmitic acid, stearic acid, oleic acid, linoleic acid and behenic acid, and naturally occurring mixtures
15 of fatty acids such as coconut fatty acid. Amidation can be carried out, for example, by reacting the polyalkylenepolyamines with alkyldiketenes.

The polyalkylenepolyamines can also be used in partially quaternized form as compounds of group (a). Examples of suitable quaternizing agents are alkyl halides
20 such as methyl chloride, ethyl chloride, butyl chloride, epichlorohydrin, hexyl chloride and benzyl chloride, and dimethyl sulfate and diethyl sulfate. If quaternized polyalkylene polyamines are employed as compound of group (a), the degree of quaternization is preferably 1 to 30, normally only up to 20,% so that sufficient free NH groups are available for reaction with the crosslinker (b).

25 Compounds of group (a) which are preferably used are polyethyleneimines with an average molecular weight of from 300 to 25,000, preferably 300 to 3000, and poly-amidoamines grafted with ethyleneimine.

30 It is likewise possible to use according to the invention polymers (a) which contain repeating units of the following formula:



These mean, in particular, oligo/polyvinylformamides and copolymers of vinylformamide in which the formamide groups are at least partly, preferably 5-100 mol%, converted into amino groups by hydrolysis. Oligo/polyvinylformamides in which the formamide groups have been 20-100 mol%, in particular 40-100 mol%, converted
5 into amino groups by hydrolysis are preferably employed. The hydrolysis can be carried out either in alkaline or in acidic medium.

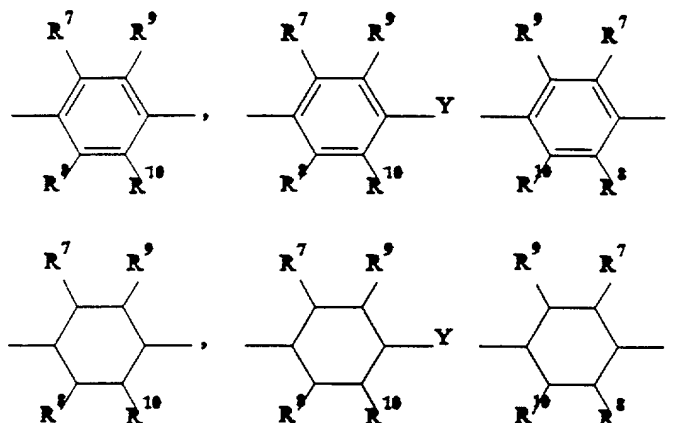
In one embodiment of the invention, these polymers have a number average molecular weight of from 80 to 150,000, preferably 100 to 50,000, particularly preferably 110 to
10 10,000, especially 129 to 5000.

The amines or polyamines used according to the invention are prepared by known processes.

15 In one embodiment of the invention, component (a) is selected from amines of the formula (II)



20 where the radicals R^1 are hydrogen atoms or $(R^2R^2)N(CH_2)_n$ - radicals,
the radicals R^2 are hydrogen atoms or $(R^3R^3)N-(CH_2)_n$ - radicals,
the radicals R^3 are hydrogen atoms or $(R^4R^4)N-(CH_2)_n$ - radicals,
the radicals R^4 are hydrogen atoms or $(R^5R^5)N-(CH_2)_n$ - radicals,
the radicals R^5 are hydrogen atoms or $(R^6R^6)N-(CH_2)_n$ - radicals,
25 the radicals R^6 are hydrogen atoms, n is 2, 3 or 4, and the radical X is one of the radicals



$-(CH_2)_p-$, $-(CH_2)_3-NR^{11}-(CH_2)_3-$, $-(CH_2)_1-[O-(CH_2)_k]_m-O-(CH_2)_1-C_{2-20}$ -alkylene,

the radical Y is an oxygen atom, a $CR^7R^9C=O$ or SO_2 radical,

p is an integer from 2-20,

1 l and k are, independently of one another, an integer from 2-6,

m is an integer from 1-40,

the radicals R^7 , R^8 , R^9 and R^{10} are, independently of one another, hydrogen atoms or C_{1-6} -alkyl radicals,

and the radical R^{11} is C_{1-20} -alkyl, C_{2-20} -dialkylamino- C_{2-10} -alkyl, C_{1-10} -alkoxy- C_{2-10} -alkyl,

10 C_{2-20} -hydroxyalkyl, C_{3-12} -cycloalkyl, C_{4-20} -cycloalkylalkyl, C_{2-20} -alkenyl, C_{4-30} -

dialkylaminoalkenyl, C_{3-30} -alkoxyalkenyl, C_{3-20} -hydroxyalkenyl, C_{5-20} -cycloalkylalkenyl,

an aryl or a C_{7-20} -arylalkyl radical which is unsubstituted or substituted one to five times

by C_{1-8} -alkyl, C_{2-8} -dialkylamino, C_{1-8} -alkoxy, hydroxyl, C_{3-8} -cycloalkyl and/or C_{4-12} -

cycloalkylalkyl, or two radicals R^{11} together form an alkylene chain which may be

15 interrupted by nitrogen or oxygen, such as from ethylene oxide, propylene oxide,

butylene oxide and $-CH_2-CH(CH_3)-O-$ or polyisobutylene with 1 to 100 isobutylene

units,

where 5-100% of the nitrogen atoms are in primary or secondary amino groups.

20 The radicals R^7 , R^8 , R^9 , R^{10} in the formula II are C_{1-6} -alkyl radicals, preferably C_{1-3} -alkyl radicals, such as methyl, ethyl, n-propyl and isopropyl radicals, particularly preferably methyl and ethyl radicals. especially methyl radicals, or preferably hydrogen, with the radicals R^7 and R^8 , and R^9 and R^{10} , preferably being identical.

Examples of radicals R^{11} according to the invention are C_{1-20} -alkyl radicals, preferably C_{1-12} -alkyl radicals such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, neopentyl, 1,2-dimethylpropyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, n-octyl, isooctyl, n-nonyl, isononyl, n-decyl, isodecyl, n-undecyl, isoundecyl, n-dodecyl and isododecyl radicals, particularly preferably C_{1-4} -alkyl radicals such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl radicals, aryl radicals such as phenyl, 1-naphthyl and 2-naphthyl radicals, preferably phenyl radicals, C_{7-20} -aralkyl radicals, preferably C_{7-12} -phenylalkyl radicals, such as benzyl, 1-phenethyl, 2-phenethyl, 1-phenylpropyl, 2-phenylpropyl, 3-phenylpropyl, 1-phenylbutyl, 2-phenylbutyl, 3-phenylbutyl and 4-phenylbutyl radicals, particularly preferably benzyl, 1-phenethyl and 2-phenethyl radicals, C_{7-20} -alkylaryl radicals, preferably C_{7-12} -alkylphenyl radicals such as 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 2,3,4-trimethylphenyl, 2,3,5-trimethylphenyl, 2,3,6-trimethylphenyl, 2,4,6-trimethylphenyl, 2-ethylphenyl, 3-ethylphenyl, 4-ethylphenyl, 2-i-propylphenyl, 3-n-propylphenyl and 4-n-propylphenyl radicals or polyisobutylene radicals with 1-100, preferably 1-70, particularly preferably 1-50, isobutylene units.

The amines of the formula (II) are preferably prepared by the process described in WO 96/15097.

They are preferably prepared from diamines of the formula $NH_2-(CH_2)_n-NH_2$ where n is an integer from 2 to 20. Examples of suitable diamines of this type are 1,2-ethylenediamine, 1,3-propylenediamine, 1,4-butylenediamine and 1,6-hexamethylenediamine. Primary tetraaminoalkylalkylenediamines are likewise preferably employed, such as N,N,N',N'-tetraaminopropyl-1,2-ethylenediamine, N,N,N',N'-tetraaminopropyl-1,3-propylenediamine, N,N,N',N'-tetraaminopropyl-1,4-butylenediamine and N,N,N',N'-tetraaminopropyl-1,6-hexamethylenediamine.

30

Preferred examples of amines (II) according to the invention, which are also referred to as dendrimeric amines, and their precursors, are N,N,N',N'-tetraaminopropylethylenediamine, referred to as N6-amine hereinafter, and the dendrimeric amines

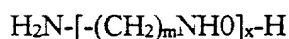
which can be prepared therefrom by aminopropylation and are referred to by the number of their nitrogen atoms, such as N14, N30, N62 and N126 amine from BASF AG. These amines have a basic ethylenediamine framework in which the hydrogen atoms on the nitrogen are replaced by amino(n-propyl)radicals. The terminal amino groups may in turn be substituted by corresponding aminopropyl groups (N14 amine) etc. Processes for preparing these amines are described in WO 96/15097, starting from ethylenediamine. Likewise preferred examples of these amines according to the invention are corresponding N amines as described in WO 93/14147, which are prepared starting from butylenediamine instead of ethylenediamine as above. Amines of this type are prepared and marketed by DsM N.V. in the Netherlands.

Further components (a) which are preferred according to the invention are polyamines of the following formula

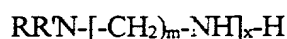


where the radicals R, R' or R'' are, independently of one another, hydrogen atoms, C₁₋₂₀-alkyl radicals, C₂₋₂₀-alkenyl radicals or C₆₋₂₀-aryl radicals, the radical R''' is a hydrogen atom or a -(CH₂)_o-[NH-(CH₂)_m]_p-NH₂ radical or a hydroxyalkyl or alkoxy radical, where x is an integer from 1-10, m is an integer from 2-4, o is an integer from 2-4, and p is an integer from 0-10.

Particularly preferred amines are those of the following formula



where m is 2, 3 or 4 and x is an integer from 1-10,



where the radicals R and R' are, independently of one another C₁₋₂₀-alkyl radicals, C₂₋₂₀-alkenyl radicals or C₆₋₂₀-aryl radicals,

m is 2, 3 or 4, and

x is an integer from 1-10,



5

where the radical R is a hydrogen atom or a C₁₋₂₀-alkyl radical, C₂₋₂₀-alkenyl radical or C₆₋₂₀-aryl radical,



10

where m is 2, 3 or 4,

o is 2, 3 or 4,

x is an integer from 0-10,

p is an integer from 0-10, and

15

the total of x and p is ≥ 1 .

Preferred compounds (a) are N,N,N',N'-tetraaminopropyl-1,2-ethylenediamine or polyethyleneimine with a degree of polymerization of from 5 to 500, preferably from 5 to 50.

20

Crosslinkers (b)

The nitrogenous compounds described above are reacted with at least one at least bifunctional crosslinker which reacts with NH groups to give crosslinked nitrogenous compounds which are soluble or dispersible in water. Crosslinkers (b) are preferably selected from the group consisting of the halogen-free crosslinkers

- (1) polyepoxides
- (2) ethylene carbonate, propylene carbonate and/or urea,
- 30 (3) monoethylenically unsaturated carboxylic acids and their esters, amides and anhydrides, at least dibasic carboxylic acids or polycarboxylic acids, and their esters, amides and anhydrides,
- (4) products of the reaction of polyetherdiamines, alkylenediamines, polyalkylene-

- polyamines, bifunctional or multifunctional alcohols, alkylene glycols, polyalkylene glycols, functionalized polyesters or polyamides or their mixtures with monoethylenically unsaturated carboxylic acids or their esters, amides or anhydrides, the reaction products having at least two ethylenic double bonds, carboxamide, carboxyl or ester groups as functional groups,
- 5
- (5) products, containing at least two aziridino groups, of the reaction of dicarboxylic esters with ethyleneimine,
 - (6) cumulenes and polyheterocumulenes,
 - (7) β -keto esters, β -keto acids and β -keto aldehydes,
 - 10 (8) functionalized glycidyl ethers,
- the halogen-containing crosslinkers
- (9) polyhalides
 - (10) glycidyl halides,
 - (11) chloroformates and chloroacetic acid derivatives,
 - 15 (12) epichlorohydrin, glycerol chlorohydrin, polyether dichlorohydrin compounds,
 - (13) phosgene
- or mixtures thereof.

Examples of polyepoxides (1) are polyalkylene glycol bisglycidyl ethers which are prepared from bischlorohydrins such as bischlorohydrins of polyethylene glycols under alkaline conditions. The alkylene glycols preferably have 2 to 10 carbon atoms, and are, in particular, ethylene glycol, 1-methylethylene glycol or 1-ethylethylene glycol.

20

It is likewise possible to use alkanediol bisglycidyl ethers, preferably of a C₂₋₁₂-alkanediol which is, in particular, linear. Examples are butanediol bisglycidyl ether and hexanediol bisglycidyl ether.

25

It is additionally possible to use aryl bisglycidyl ethers and cyclic alkyl bisglycidyl ethers which are derived, in particular, from benzene nuclei or dimethylcyclohexane nuclei, which may in turn be substituted. It is likewise possible to use bisepoxides such as bis-ethylene oxide and ethylene oxide units which are separated by a linear C₁₋₁₂-alkylene radical.

30

Preferably employed from group (2), ethylene carbonate, propylene carbonate and/or urea, is propylene carbonate.

5 Monoethylenically unsaturated carboxylic acids and their esters, amides and anhydrides from group (3) are, for example, acrylic acid, methacrylic acid, crotonic acid, acrylates or acrylamides from primary or secondary amines. The alcohol residue has in this case 1 to 22, preferably 1 to 18, carbon atoms, and the amine residue 0 to 12 carbon atoms. At least dibasic carboxylic acids or polycarboxylic acids can be either saturated or unsaturated. Examples are tartaric acid and its analogs, and C₂₋₅₀-dicarboxylic acids, in
10 particular linear C₂₋₅₀-alkylenedicarboxylic acids, and their esters, amides or anhydrides. Esters or diesters can be formed with C₁₋₂₂-alcohols, and amides and diamides may have C₁₋₂₂ radicals.

15 Examples of suitable dicarboxylic esters are dimethyl oxalate, diethyl oxalate, diisopropyl oxalate, dimethyl succinate, diethyl succinate, diisopropyl succinate, di-n-propyl succinate, diisobutyl succinate, dimethyl adipate, diethyl adipate and diisopropyl adipate.

20 Examples of unsaturated acids are maleic acid, itaconic acid and their anhydrides or esters.

25 Examples of polycarboxylic acids are citric acid, propanetricarboxylic acid, ethylenediaminetetraacetic acid, butanetetracarboxylic acid, and higher polycarboxylic acids. It is also possible to use polymers of methacrylic acid, maleic acid, itaconic acid or mixtures thereof. It is also possible to employ copolymers with C₂₋₃₀-olefins, such as copolymers of maleic anhydride and isobutene or diisobutene. The anhydride groups may moreover be converted into esters or amides. Examples of suitable polymers are described in EP-A 0 276 464, US 3,810,834, GB-A 1 411 063 and US 4,818,795.

30 It is furthermore possible to employ salts of all the acids mentioned.

Examples of group (4) are polyetherdiacrylic acid, -diacrylic esters and -diacrylamides, for example compounds which have 1 to 50 ethylene oxide units and in which the

alcohol residue in the ester has 1 to 22 carbon atoms, and the amides which can be formed from ammonia, primary or secondary amines with C₁₋₂₂ radicals. Other examples are ethylenediaminediacrylates and polyetherdiaminediacrylates. The alcohol residues in the acrylates once again have 1 to 22 carbon atoms, and the polyether portion can have 0 to 50 repeating units. Apart from ethylene oxide units, the polyether block can also be composed of propylene oxide units or THF units. One example is a poly-THF-diaminediacrylate or -acrylamide or acrylic acid. The amine functionalities may also be derived from the amines mentioned at the outset.

10 The acrylate groups are in this case bonded to the amine groups by Michael addition. They may also be linked by amide formation with the amine groups of the polyether diamines, so that the molecules have two ethylenically unsaturated groups. Poly-THF-diacrylamides can be used correspondingly. It is furthermore possible to use polyiminedi- and -polyacrylates in which two or more NH groups are added onto
15 acrylates by Michael additions. It is possible to use correspondingly polyaminediacrylates and polyimine-MA-monoamides or polyamine-MA-monoamides. In these cases, the terminal amino groups in the polyimine or polyamine are in each case reacted with one molecule of maleic anhydride (MA) to give the corresponding monoamides. The remaining acid functionalities in the maleic acid can in this case be
20 replaced by esters or amides. It is likewise possible to use a polyether diamine dimaleic monoamide, ie. a polyetherdiamine whose two terminal amino groups have each been reacted with one maleic anhydride molecule to give an amide. The remaining acid functionalities of the maleic anhydride may likewise be in the form of esters or amides. The polyether diamines, polyimines or polyamines preferably have 5 to 50 repeating
25 units.

The resulting products should in general have at least two ethylenic double bonds, carboxamide, carboxyl or ester groups as functional groups. Products of the reactions of amines or glycols with maleic anhydride, such as alkylene glycols, polyethylene glycols, polyethyleneimines or polypropyleneimines preferably have molecular weights
30 in the range from 400 to 100,000. Products of the reaction of maleic anhydride with α,ω -polyetherdiamines with a molecular weight of from 400 to 5000, products of the reaction of polyethyleneimines with a molecular weight of from 129 to 50,000 with

maleic anhydride, and products of the reaction of ethylenediamine or triethylenetetramine with maleic anhydride in the molar ratio not exceeding 1.2 are particularly preferred. The polyetherdiamines, alkylenediamines and polyalkylenepolyamines can also be reacted with maleic anhydride in a Michael addition.

Examples of compounds of group (5) are products of the reaction of C_{2-50} -dicarboxylic acids, especially linear alkylenedicarboxylic acids, with ethyleneimine. One example is α -1-aziridinoethyloxamide.

Examples of cumulenes and polyheterocumulenes of group (6) are 2,6-tolylene diisocyanate, 2,4-tolylene diisocyanate and compounds of the formulae $O=C=N-X-N=C=O$ and $S=C=N-X-N=C=S$, where X is a C_{1-22} -alkylene radical or C_{6-20} -arylene radical.

β -Keto esters, β -keto acids and β -keto aldehydes (7) may have the formula $R^1-C(=O)-CR^2R^3-C(=O)-R^4$ where the radicals R^1 to R^3 can be hydrogen atoms or C_{1-12} -alkyl radicals, and R^4 can be hydrogen, OH or a C_{1-22} -alkoxy radical.

Examples of functionalized glycidyl ethers (8) are glycidyl acrylate or 2-propenyl glycidyl ether.

Examples of halogen-containing crosslinkers are polyhalides (9) such as linear C_{1-10} -alkylene dichlorides, such as dichloromethane or 1,2-dichloroethane. The polyhalides may also be derived from polyethylene oxides or ethylene oxides substituted by methyl or ethyl radicals. They may likewise be present in poly-THF molecules, in which case the halides are at the ends of the polymer chain. It is moreover possible to use random polymers or block copolymers of corresponding polyethers which have two halogen atoms. The weight average molecular weight is preferably 300 to 3000.

Glycidyl halides (10) which can be used are epichlorohydrin and glycidyl ethers of haloalkanes or aromatic halogen compounds. The halogen atoms of the crosslinkers (9) and (10) and of the following crosslinkers are preferably chlorine atoms or bromine

atoms, in particular chlorine atoms.

Glycerol chlorohydrin and polyether dichlorohydrin compounds (12) are prepared from epichlorohydrin and the appropriate alcohols, ie. glycerol or polyethylene glycols. The polymeric crosslinkers generally have a weight average molecular weight of from 100 to 10,000, preferably 300 to 3000. Particularly preferred crosslinkers are bischlorohydrins and bisglycidyl ethers of polyethylene glycols. The bisglycidyl ethers can be prepared under alkaline conditions.

10 Preparation of the crosslinked nitrogenous compounds

The water-soluble reaction products according to the invention can be obtained by reacting the compounds of components (a) with the crosslinkers of component (b). The reaction is preferably carried out in aqueous medium. Condensation of components (a) and (b) is carried out, for example, at a temperature in the range from 0 to 200°C, preferably 20 to 160°C. If the condensation is carried out in an aqueous solution at temperatures above the boiling point of water, the reaction is undertaken in pressure-tight apparatus. However, the condensation can also be carried out without diluent or in solvents which are inert to the reactants, such as high-boiling ethers (diethylene glycol dimethyl ether), tetrahydrofuran, polyols, toluene, xylenes, other high-boiling substituted aromatic compounds or commercial hydrocarbon fractions boiling in the range from 50 to 300°C. In the case of condensation in aqueous solution, the pH of the reaction mixture is, for example, 2 to 12, preferably 5 to 11. In most cases, condensation is carried out at the pH set up when the reactants dissolve in the water. The concentration of the resulting water-soluble condensates in the aqueous solution is, for example, 10 to 90% by weight and is preferably in the range from 20 to 80% by weight. The reaction products are regarded as soluble in water when they are able to form a solution with a strength of at least 5% by weight in water at room temperature. Condensation of the compounds of components (a) and (b) is preferably carried out in aqueous solution so as to result in water-soluble condensates which, in a 20% by weight aqueous solution at 20°C, have a viscosity of at least 100 mPas, preferably 100 to 15,000 mPas (measured at pH 7 in a Brookfield viscometer).

The mixtures reacted in the condensation contain from 50 to 99.9% by weight, preferably 60 to 99.5% by weight, of at least one compound of component (a) and from 0.1 to 50% by weight, preferably 0.5 to 40% by weight, of at least one compound of component (b), with the total of components (a) and (b) always being 100% by weight.

The result, especially when oligoamines or polyamines and bisfunctionalized polyethylene glycol blocks are used, is, depending on the reaction conditions and molar ratio, a polymer with a network structure consisting of amine and polyethylene glycol blocks of defined size, chain length and molecular weight distribution. The compounds according to the invention improve the detachment of soil in the washing of textiles on the one hand due to the soil release properties, and on the other hand due to the enzyme-stabilizing effect, which increases the activity of the enzymes. Enzymes present in modern detergents, such as proteases, lipases, cellulases, amylases and peroxidases, which are used to improve the detergency performance, are exposed to destabilizing and inactivating conditions in the detergent formulation. These conditions may be caused by various ingredients in the formulation, such as the surfactant system, the bleach system, the alkalis etc. This problem is common in liquid detergent formulations in particular, because the enzymes are not protected from contact owing to the mobility of the detergent ingredients. In this case, the crosslinked compounds according to the invention result in a stabilization and retention of the enzymes, which are thus able to display their full effect in the washing process.

Addition of even small amounts of the crosslinked nitrogenous compounds according to the invention, especially the crosslinked polyamines, improves the soil-releasing properties of color detergent, heavy duty detergent or compact detergent formulations. The compounds according to the invention are probably adsorbed from the wash liquor onto the textiles. When a textile treated in this way is soiled, the compounds applied to the textile result in a distinctly improved detachment of soil in the subsequent wash. The compounds according to the invention are particularly effective for stains consisting of a combination of fatty or oily soil and pigment particles, for example stains consisting of used engine oil, lipstick, makeup or shoe cream. The compounds are particularly advantageous for cleaning polyester fabrics or polyester-containing

fabrics.

The invention thus also relates to detergents and cleaners comprising at least one crosslinked nitrogenous compound as defined above, and at least one surfactant. The detergent and cleaner preferably comprises at least one enzyme in addition.

These detergents can be used according to the invention for washing textiles.

The detergents according to the invention may furthermore comprise the ingredients conventionally used in detergents, such as builders, surfactants, bleaches, enzymes and other ingredients as described hereinafter.

Builders

Inorganic builders (A) suitable for combination with the (polyalkylenepoly)amines according to the invention are, in particular, crystalline or amorphous aluminosilicates with ion-exchanging properties such as, in particular, zeolites. Various types of zeolites are suitable, in particular zeolites A, X, B, P, MAP and HS in their Na form or in forms in which Na is partly replaced by other cations such as Li, K, Ca, Mg or ammonium. Suitable zeolites are described, for example, in EP-A 038591, EP-A 021491, EP-A 087035, US-A 4604224, GB-A 2013259, EP-A 522726, EP-A 384070 and WO-A 94/24251.

Examples of suitable crystalline silicates (A) are disilicates or sheet silicates, eg. SKS-6 (manufactured by Hoechst AG). The silicates can be employed in the form of their alkali metal, alkaline earth metal or ammonium salts, preferably as Na, Li and Mg silicates.

Amorphous silicates such as sodium metasilicate with a polymeric structure, or Britesil® H20 (manufactured by Akzo N.V. in the Netherlands) can likewise be used.

Suitable carbonate-based inorganic builders are carbonates and bicarbonates. These can be employed in the form of their alkali metal, alkaline earth metal or ammonium salts.

Na, Li and Mg carbonates and bicarbonates, especially sodium carbonate and/or sodium bicarbonate, are preferably employed.

5 Phosphates usual as inorganic builders are polyphosphates. eg. pentasodium triphosphate.

Said components (A) can be employed singly or in mixtures with one another. An inorganic builder component of particular interest is a mixture of aluminosilicates and carbonates, especially of zeolites, in particular zeolite A, and alkali metal carbonates, in particular sodium carbonate, in the ratio of from 98:2 to 20:80, in particular from 85:15 to 40:60, by weight. Other components (A) may also be present in addition to this mixture.

15 In a preferred embodiment, the textile detergent formulation according to the invention contains 0.1 to 20% by weight, in particular 1 to 12% by weight, of organic cobuilders (B) in the form of low molecular weight oligomeric or polymeric carboxylic acids, especially polycarboxylic acids, or phosphonic acids or their salts, in particular Na or K salts.

20 Examples of suitable low molecular weight carboxylic acids or phosphonic acids for (B) are:

C₄-C₂₀-di-, -tri- and -tetracarboxylic acids such as succinic acid, propanetricarboxylic acid, butanetetracarboxylic acid, cyclopentanetetracarboxylic acid and alkyl- and alkenylsuccinic acids with C₂-C₁₆-alkyl and -alkenyl radicals respectively;

C₄-C₂₀-hydroxy carboxylic acids such as malic acid, tartaric acid, gluconic acid, glutaric acid, citric acid, lactobionic acid and sucrosemono-, -di- and -tricarboxylic acids;

30 aminopolycarboxylic acids such as nitrilotriacetic acid, β -alaninediacetic acid, ethylenediaminetetraacetic acid, serinediacetic acid, isoserinediacetic acid, methylglycinediacetic acid and alkylethylenediaminetriacetates;

salts of phosphonic acids such as hydroxyethanediphosphonic acid.

Examples of suitable oligomeric or polymeric carboxylic acids for (B) are:

5 Oligomaleic acids as described, for example, in EP-A 0 451 508 and EP-A 0 396 303;

co- and terpolymers of unsaturated C₄-C₈-dicarboxylic acids, possible comonomers being monoethylenically unsaturated monomers

10 from group (i) in amounts of up to 95% by weight,
from group (ii) in amounts of up to 60% by weight and
from group (iii) in amounts of up to 20% by weight.

Examples of suitable unsaturated C₄-C₈-dicarboxylic acids in this case are maleic acid,
15 fumaric acid, itaconic acid and citraconic acid. Maleic acid is preferred.

Group (i) comprises monoethylenically unsaturated C₃-C₈-monocarboxylic acids such as acrylic acid, methacrylic acid, crotonic acid and vinylacetic acid. Preferably employed from group (i) are acrylic acid and methacrylic acid.

20 Group (ii) comprises monoethylenically unsaturated C₂-C₂₂-olefins, vinyl alkyl ethers with C₁-C₈-alkyl groups, styrene, vinyl esters of C₁-C₈-carboxylic acids, (meth)-acrylamide and vinylpyrrolidone. Preferably employed from group (ii) are C₂-C₆-olefins, vinyl alkyl ethers with C₁-C₄-alkyl groups, vinyl acetate and vinyl propionate.

25 Group (iii) comprises (meth)acrylic esters of C₁-C₈-alcohols, (meth)acrylonitrile, (meth)acrylamides of C₁-C₈-amines, N-vinylformamide and vinylimidazole.

30 If the group (ii) polymers contain vinyl ester units, these can also be partly or completely hydrolyzed to vinyl alcohol structural units. Suitable co- and terpolymers are disclosed, for example, in US-A 3 887 806 and DE-A 43 13 909.

Suitable and preferred copolymers of dicarboxylic acids for component (B) are:

copolymers of maleic acid and acrylic acid in the ratio 100:90 to 95:5 by weight, particularly preferably those in the ratio 30:70 to 90:10 by weight, with molecular weights of from 100,000 to 150,000:

5 terpolymers of maleic acid, acrylic acid and a vinyl ester of a C₁-C₃-carboxylic acid in the ratio 10 (maleic acid):90 (acrylic acid + vinyl ester) to 95 (maleic acid):10 (acrylic acid + vinyl ester) by weight, it being possible for the ratio of acrylic acid to the vinyl ester to vary in the range from 30:70 to 70:30 by weight;

10 copolymers of maleic acid with C₂-C₈-olefins in the molar ratio 40:60 to 80:20, with copolymers of maleic acid with ethylene, propylene or isobutylene in the molar ratio 50:50 being particularly preferred.

Graft copolymers of unsaturated carboxylic acids on low molecular weight carbohydrates or hydrogenated carbohydrates, cf. US-A 5 227 446, DE-A 44 15 623
15 and DE-A 43 13 909, are likewise suitable as component (B).

Examples of suitable unsaturated carboxylic acids in this case are maleic acid, fumaric
acid, itaconic acid, citraconic acid, acrylic acid, methacrylic acid, crotonic acid and
20 vinylacetic acid, and mixtures of acrylic acid and maleic acid, which are grafted on in amounts of from 40 to 95% of the weight of the component to be grafted.

It is additionally possible for up to 30% by weight, based on the component to be grafted, of other monoethylenically unsaturated monomer units to be present in the
25 polymer for modification. Suitable modifying monomers are the abovementioned monomers of groups (ii) and (iii).

Suitable as grafting base are degraded polysaccharides such as acidically or enzymatically degraded starches, inulins or cellulose, protein hydrolysates and reduced
30 (hydrogenated or reductively aminated) degraded polysaccharides such as mannitol, sorbitol, aminosorbitol and N-alkylglucamine, and polyalkylene glycols with molecular weights of up to M_w = 5000, such as polyethylene glycols, ethylene oxide/propylene oxide or ethylene oxide/butylene oxide or ethylene oxide/propylene oxide/butylene

oxide block copolymers and alkoxylated monohydric or polyhydric C₁-C₂₂-alcohols. cf. US-A 5 756 456.

5 Preferably employed from this group are grafted degraded or degraded reduced starches and grafted polyethylene oxides, employing 20 to 80% by weight of monomers based on the grafting component in the graft copolymerization. A mixture of maleic acid and acrylic acid in the ratio from 90:10 to 10:90 by weight is preferably employed for the grafting.

10 Polyglyoxylic acids suitable as component (B) are described, for example, in EP-B 0 001 004, US-A 5 399 286, DE-A 41 06 355 and EP-A 0 656 914. The endgroups of the polyglyoxylic acids may have different structures.

15 Polyamidocarboxylic acids and modified polyamidocarboxylic acids suitable as component (B) are disclosed, for example, in EP-A 0 454 126, EP-B 0 511 037, WO-A 94/01486 and EP-A 0 581 452.

20 Also particularly used as component (B) are polyaspartic acids or cocondensates of aspartic acid with other amino acids, C₄-C₂₅-mono- or -dicarboxylic acids and/or C₄-C₂₅-mono- or -diamines. Particularly preferably employed are polyaspartic acids prepared in phosphorus-containing acids and modified with C₆-C₂₂-mono- or dicarboxylic acids or with C₆-C₂₂-mono- or -diamines.

25 Condensates of citric acid with hydroxy carboxylic acids or polyhydroxy compounds suitable as component (B) are disclosed, for example, in WO-A 93/22362 and WO-A 92/16493. Carboxyl-containing condensates of this type normally have molecular weights of up to 10,000, preferably up to 5000.

30 Also suitable as component (B) are ethylenediaminedisuccinic acid, oxydisuccinic acid, aminopolycarboxylates, aminopolyalkylenephosphonates and polyglutamates.

Oxidized starches can also be used as organic cobuilders in addition to component (B).

Surfactants

Suitable anionic surfactants (C) are, for example, fatty alcohol sulfates of fatty alcohols with 8 to 22, preferably 10 to 18, carbon atoms, eg. C₉-C₁₁-alcohol sulfates, C₁₂-C₁₄-alcohol sulfates, cetyl sulfate, myristyl sulfate, palmityl sulfate, stearyl sulfate and tallow fatty alcohol sulfate.

Other suitable anionic surfactants are sulfated ethoxylated C₈-C₂₂-alcohols (alkyl ether sulfates) and their soluble salts. Compounds of this type are prepared, for example, by initially alkoxyating a C₈-C₂₂, preferably a C₁₀-C₁₈, alcohol, eg. a fatty alcohol, and subsequently sulfating the alkoxylation product. Ethylene oxide is preferably used for the alkoxylation, in which case 2 to 50, preferably 3 to 20, mol of ethylene oxide are employed per mole of alcohol. However, the alcohols can also be alkoxyated with propylene oxide, alone or with butylene oxide. Also suitable are those alkoxyated C₈-C₂₂-alcohols which contain ethylene oxide and propylene oxide or ethylene oxide and butylene oxide or ethylene oxide and propylene oxide and butylene oxide. The alkoxyated C₈-C₂₂-alcohols may contain the ethylene oxide, propylene oxide and butylene oxide units in the form of blocks or in random distribution. Alkyl ether sulfates with a wide or narrow alkylene oxide distribution can be obtained depending on the nature of the alkoxylation catalyst.

Other suitable anionic surfactants are alkanesulfonates such as C₈-C₂₄, preferably C₁₀-C₁₈, alkanesulfonates, and soaps such as the Na and K salts of C₈-C₂₄-carboxylic acids.

Further suitable anionic surfactants are linear C₉-C₂₀ alkylbenzenesulfonates (LAS) and -alkyltoluenesulfonates.

Also suitable as anionic surfactants (C) are C₈-C₂₄-olefinsulfonates and -disulfonates which may also represent mixtures of alkene- and hydroxyalkanesulfonates and -disulfonates, alkyl ester sulfonates, sulfonated polycarboxylic acids, alkylglycerol sulfonates, fatty acid glycerol ester sulfonates, alkylphenol polyglycol ether sulfates, paraffinsulfonates with about 20 to about 50 carbon atoms (based on paraffin or paraffin mixtures obtained from natural sources), alkyl phosphates, acylisethionates,

acyltaurates, acylmethyлтаurates, alkylsuccinic acids, alkenylsuccinic acids or their monoesters or monoamides, alkylsulfosuccinic acids or their amides, mono- and diesters of sulfosuccinic acids, acylsarcosinates, sulfated alkyl polyglucosides, alkylpolyglycol carboxylates and hydroxyalkylsarcosinates.

5

The anionic surfactants are added to the detergents preferably in the form of salts. Suitable cations in the salts are alkali metal ions such as sodium, potassium, lithium and ammonium ions, eg. hydroxyethylammonium, di(hydroxyethyl)ammonium and tri(hydroxyethyl)ammonium ions.

10

Component (C) is preferably present in the textile detergent formulation according to the invention in an amount of from 3 to 30% by weight, in particular 5 to 15% by weight. If linear C₉-C₂₀-alkylbenzenesulfonates (LAS) are present, these are normally used in an amount of up to 10% by weight, in particular up to 8% by weight. It is possible to employ only one class of anionic surfactants alone, for example only fatty alcohol sulfates or only alkylbenzenesulfonates, but mixtures of various classes can also be used, eg. a mixture of fatty alcohol sulfates and alkylbenzenesulfonates. Mixtures of different species within individual classes of anionic surfactants may also be employed.

15

20

Examples of suitable nonionic surfactants (D) are alkoxyated C₈-C₂₂-alcohols such as fatty alcohol alkoxyates or oxoalcoholalkoxyates. The alkoxylation can be carried out with ethylene oxide, propylene oxide and/or butylene oxide. Surfactants which can be employed in this case are all alkoxyated alcohols which contain at least two molecules of an abovementioned alkylene oxide in the adduct. Once again, block copolymers of ethylene oxide, propylene oxide and/or butylene oxide are suitable, or adducts which contain said alkylene oxides in random distribution. From 2 to 50, preferably 3 to 20, mol of at least one alkylene oxide are used per mole of alcohol. Ethylene oxide is preferably employed as alkylene oxide. The alcohols preferably have 10 to 18 carbon atoms. Alkoxyates with a wide or narrow alkylene oxide distribution can be obtained depending on the nature of the alkoxylation catalyst.

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Another class of suitable nonionic surfactants comprises alkylphenol alkoxyates such as alkylphenol ethoxyates with C₆-C₁₄-alkyl chains and 5 to 30 mol of alkylene oxide

units.

Another class of nonionic surfactants comprises alkyl polyglucosides or hydroxyalkyl polyglucosides with 8 to 22, preferably 10 to 18, carbon atoms in the alkyl chain. These compounds usually contain 1 to 20, preferably 1.1 to 5, glucoside units.

Another class of nonionic surfactants comprises N-alkylglucamides with C₆-C₂₂-alkyl chains. Compounds of this type are obtained, for example, by acylation of reductively aminated sugars with appropriate long-chain carboxylic acid derivatives.

Also suitable as nonionic surfactants (D) are block copolymers of ethylene oxide, propylene oxide and/or butylene oxide (Pluronic® and Tetronic® brands of BASF AG), polyhydroxy or polyalkoxy fatty acid derivatives such as polyhydroxy fatty amides, N-alkoxy or N-aryloxy-polyhydroxy fatty amides, fatty amide ethoxylates, especially endgroup-capped and fatty alkanolamide alkoxylates.

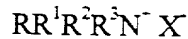
Component (D) is preferably present in the textile detergent formulation according to the invention in an amount of from 1 to 20% by weight, in particular 3 to 12% by weight. It is possible to employ only one class of nonionic surfactants, in particular only alkoxylated C₈-C₂₂-alcohols, but mixtures of various classes can also be used. Mixtures of different species within the individual classes of nonionic surfactants can also be employed.

Since the balance between the types of surfactants mentioned is of significance for the activity of the detergent formulation according to the invention, the ratio by weight of anionic surfactants (C) to nonionic surfactants (D) is preferably from 95:5 to 20:80, in particular from 70:30 to 50:50.

The detergents according to the invention can furthermore also contain cationic surfactants (E).

Examples of suitable cationic surfactants are surface-active compounds containing ammonium groups, such as alkyldimethylammonium halides and compounds of the

formula



5 where the radicals R to R³ are alkyl, aryl, alkylalkoxy, arylalkoxy, hydroxyalkyl(alkoxy), hydroxyaryl(alkoxy) groups and X is a suitable anion.

The detergents according to the invention may also contain ampholytic surfactants (F), such as aliphatic derivatives of secondary or tertiary amines which contain in one of the
10 side chains an anionic group, alkyldimethylamine oxides or alkyl- or alkoxymethylamine oxides.

Components (E) and (F) may comprise up to 25%, preferably 3-15%, in the detergent
15 formulation.

Bleaches

In another preferred embodiment, the textile detergent formulation according to the invention additionally contains 0.5 to 30% by weight, in particular 5 to 27% by weight,
20 especially 10 to 23% by weight, of bleach (G). Examples are alkali metal perborates or alkali metal carbonate perhydrates, especially the sodium salts.

One example of an organic peracid which can be used is peracetic acid, which is preferably used in commercial textile laundry or commercial cleaning.

25 Bleach or textile detergent compositions which can advantageously be used contain C₁₋₁₂-percarboxylic acids, C₈₋₁₆-dipercarboxylic acids, imidopercaproic acids, or aryldipercaproic acids. Preferred examples of acids which can be used are peracetic acid, linear or branched peroctanoic, -nonanoic, -decanoic or -dodecanoic acids,
30 diperdecanedioic and -dodecanedioic acids, mono- and diperphthalic acids, -isophthalic acids and -terephthalic acids, phthalimidopercaproic acid and terephthaloyldipercaproic acid. It is likewise possible to use polymeric peracids, for example those containing acrylic acid basic units in which a peroxy functionality is present. The percarboxylic

acids can be used as free acids or as salts of the acids, preferably alkali metal or alkaline earth metal salts. These bleaches (G) may be used in combination with from 0 to 15% by weight, preferably 0.1 to 15% by weight, in particular 0.5 to 8% by weight, of bleach activators (H). The bleach (G) is (if present) employed in color detergents as a rule without bleach activator (H), otherwise bleach activators (H) are also usually present.

Suitable bleach activators (H) are:

- 10 - polyacylated sugars, eg. pentaacetylglucose;
- acyloxybenzenesulfonic acids and their alkali metal and alkaline earth metal salts, eg. sodium p-isononanoyloxybenzenesulfonate or sodium p-benzoyloxybenzenesulfonate;
- N,N-diacylated and N,N,N',N'-tetraacylated amines, eg. N,N,N',N'-tetraacetylmethylenediamine and -ethylenediamine (TAED), N,N-diacetylaniline, N,N,-diacetyl-p-toluidine or 1,3-diacylated hydantoins such as 1,3-diacetyl-5,5-dimethylhydantoin;
- 15 - N-alkyl-N-sulfonylcarboxamides, eg. N-methyl-N-mesylacetamide or N-methyl-N-mesylbenzamide;
- 20 - N-acylated cyclic hydrazides, acylated triazoles or urazoles, eg. monoacetylated maleic hydrazides;
- O,N,N-trisubstituted hydroxylamines, eg. O-benzoyl-N,N-succinylhydroxylamine, O-acetyl-N,N-succinylhydroxylamine or O,N,N-triacetylhydroxylamine;
- 25 - N,N'-diacylsulfamides, eg. N,N'-dimethyl-N,N'-diacetylsulfamide or N,N'-diethyl-N,N'-dipropionylsulfamide;
- triacylcyanurates, eg. triacetylcyanurate or tribenzoylcyanurate;
- carboxylic anhydrides, eg. benzoic anhydride, m-chlorobenzoic anhydride or phthalic anhydride;
- 30 - 1,3-diacyl-4,5-diacyloxyimidazolines, eg. 1,3-diacetyl-4,5-diacetoxyimidazoline;
- tetraacetylglycoluril and tetrapropionylglycoluril;
- diacylated 2,5-diketopiperazines, eg. 1,4-diacetyl-2,5-diketopiperazine;

- products of the acylation of propylenediurea and 2.2-dimethylpropylenediurea, eg. tetraacetylpropylenediurea;
- α -acyloxypolyacetylmalonamides, eg. α -acetoxym-N,N'-diacetylmalonamide;
- diacyldioxohexahydro-1,3,5-triazines, eg. 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine;
- benzo(4H)-1,3-oxazin-4-ones with alkyl radicals, eg. methyl, or aromatic radicals, eg. phenyl, in position 2.

The described bleach system consisting of bleach and bleach activators may also contain bleach catalysts. Examples of suitable bleach catalysts are quaternized imines and sulfone imines which are described, for example, in US-A 5 360 569 and EP-A 0 453 003. Particularly effective bleach catalysts are manganese complexes which are described, for example, in WO-A 94/21777. Compounds of this type are, if they are used, incorporated into the detergent formulations in amounts not exceeding 1.5% by weight, in particular up to 0.5% by weight. Bleach catalysts which can likewise be used are the amines described in the application filed at the same time as this application and entitled "Bleach boosters for bleach and textile detergent compositions".

Besides the described bleach system consisting of bleaches and bleach activators with or without bleach catalysts, the use of systems with enzymatic release of peroxide or of photoactivated bleach systems for the textile detergent formulation according to the invention is also conceivable.

Enzymes

In another preferred embodiment, the textile detergent formulation according to the invention additionally contains 0.05 to 4% by weight of enzymes (J). Enzymes which are preferably employed in detergents are proteases, amylases, lipases and cellulases. The amounts of enzymes added are preferably 0.1-1.5% by weight, in particular preferably 0.2 to 1.0% by weight, of the formulated enzyme. Examples of suitable proteases are Savinase and Esperase (manufactured by Novo Nordisk). An example of a suitable lipase is Lipolase (manufactured by Novo Nordisk). An example of a suitable cellulase is Celluzym (manufactured by Novo Nordisk). It is also possible to use

peroxidases to activate the bleach system. Single enzymes or a combination of different enzymes can be employed. The textile detergent formulation may also contain enzyme stabilizers, eg. calcium propionate, sodium formate or boric acids or their salts, and/or oxidation inhibitors.

5

Other ingredients

The textile detergent formulation according to the invention may, besides the main components (A) to (J) mentioned, also contain the following other conventional additives in the amounts customary for this purpose:

10

- antiredeposition agents and other soil release polymers

15

Suitable other soil release polymers and/or antiredeposition agents for detergents are, for example:

20

polyesters from polyethylene oxides with ethylene glycol and/or propylene glycol and aromatic dicarboxylic acids or aromatic and aliphatic dicarboxylic acids;

25

polyesters from polyethylene oxides endgroup-capped at one end with dihydric and/or polyhydric alcohols and dicarboxylic acid.

Polyesters of this type are disclosed, for example, in US-A 3,557,039, GB-A 1 154 730, EP-A-0 185 427, EP-A-0 241 984, EP-A-0 241 985, EP-A-0 272 033 and US-A 5,142,020.

30

Other suitable soil release polymers are amphiphilic graft or other copolymers of vinyl and/or acrylic esters on polyalkylene oxides (cf. US-A 4,746,456, US-A 4,846,995, DE-A-37 11 299, US-A 4,904,408, US-A 4,846,994 and US-A 4,849,126), or modified celluloses such as methylcellulose, hydroxypropylcellulose or carboxymethylcellulose.

- Color transfer inhibitors, for example homo- and copolymers of vinylpyrrolidone, of vinylimidazole, of vinyloxazolidone or of 4-vinylpyridine N-oxide with molecular weights of from 15,000 to 100,000, and crosslinked fine-particle polymers based on these monomers;
- 5 - non-surfactant foam suppressants or foam inhibitors, for example organopolysiloxanes and their mixtures with microfine, possibly silanized silica, and paraffins, waxes, microcrystalline waxes and their mixtures with silanized silica;
- complexing agents (also acting as organic cobuilders);
- 10 - optical brighteners;
- polyethylene glycols;
- perfumes or fragrances;
- bulking agents;
- inorganic fillers, eg. sodium sulfate;
- 15 - formulation aids;
- solubility improvers;
- opacifying and pearlescent agents;
- dyes;
- corrosion inhibitors;
- 20 - peroxide stabilizers;
- electrolytes.

The detergent formulation according to the invention is solid, ie. is normally in the form of a powder or granules, or an extrudate or tablet.

25

The powder or granular detergents according to the invention may contain up to 60% by weight of inorganic fillers. Sodium sulfate is normally used for this purpose. However, the detergents according to the invention preferably contain only up to 20% by weight, particularly preferably only up to 8% by weight, of fillers, especially in the

30 case of compact or ultracompact detergents. The solid detergents according to the invention may have bulk densities varying in the range from 300 to 1300 g/l, in particular from 550 to 1200 g/l. Modern compact detergents usually have high bulk densities and a granular structure. The processes customary in the industry can be

employed for the required compaction of the detergents.

The detergent formulation according to the invention is produced and, where appropriate, formulated by conventional methods.

5

Typical compositions of compact heavy duty detergents and color detergents are indicated below (the percentage data hereinafter and in the examples are based on weight; the data in parentheses for the compositions are preferred ranges):

10 *Composition of compact heavy duty detergents (powder or granule form)*

1-60% (8-30%) of at least one anionic (C) and one nonionic surfactant (D)

15 5-50% (10-45%) of at least one inorganic builder (A)

0.1-20% (0.5-15%) of at least one organic cobuilder (B)

5-30% (10-25%) of an inorganic bleach (G)

20

0.1-15% (1-8%) of a bleach activator (G)

0-1% (max. 0.5%) of a bleach catalyst

25 0.05-5% (0.2-2.5%) of a color transfer inhibitor

0.3-1.5% of a soil release agent according to the invention

0.1-4% (0.2-2%) of enzyme or enzyme mixture (H)

30

Other conventional additives:

sodium sulfate, complexing agents, phosphonates, optical brighteners, perfume oils, foam suppressants, antireposition agents, bleach stabilizers

Composition of color detergents (powder or granule form)

- 3-50% (8-30%) of at least one anionic (C) and one nonionic surfactant (D)
- 5 10-60% (20-55%) of at least one inorganic builder (A)
- 0-15% (0-5%) of an inorganic bleach (G)
- 10 0.05%-5% (0.2-2.5%) of a color transfer inhibitor
- 0.1-20% (1-8%) of at least one organic cobuilder (B)
- 0.2-2% of enzyme or enzyme mixture (J)
- 15 0.2-1.5% of soil release agent according to the invention

Other conventional additives:

- sodium sulfate, complexing agents, phosphonates, optical brighteners, perfume oils,
- 20 foam suppressants, antireposition agents, bleach stabilizers.

The crosslinked nitrogenous compounds according to the invention (soil release agents) are present in detergents according to the invention in amounts of from 0.05 to 5% by weight, preferably 0.1 to 4% by weight, in particular 0.2 to 2% by weight.

25

The invention is explained in detail by means of the following examples.

Examples

30 General method 1:

Crosslinking of polyethyleneimine or polyethyleneimine derivatives with the bisglycidyl ether of a polyethylene glycol of molecular weight 1500

A 20 to 22% strength aqueous solution of a polyethylene glycol bisglycidyl ether of average molecular weight 1600 (or its bischlorohydrin) is added in portions to a 25% strength aqueous solution of the polyethyleneimine or derivative at 70°C until the reaction solution has a viscosity of about 500 to 1000 mPas. The pH of the solution is
5 adjusted to 7.5 to 8.0 with 85% strength formic acid.

This general method can be applied, for example, to polyethyleneimines and their amidation products.

10 Example A

Polyethyleneimine from 10 mol of ethyleneimine crosslinked with bisglycidylether of a polyethylene glycol of molecular weight 1500

15 A 60% strength ethyleneimine solution composed of 43 g (1 mol) of ethyleneimine and 29 g of ice is added dropwise to a catalyst solution composed of 6.0 g (0.10 mol) of ethylenediamine, 2.2 g (0.05 mol) of CO₂ and 17 g of deionized water at 90°C. The mixture is then stirred at 90°C until the Preußmann test* for alkylating substances is negative. The product obtained in this way is crosslinked with the bisglycidyl ether by
20 general method 1.

Example B

25 Polyethyleneimine from 20 mol of ethyleneimine crosslinked with bisglycidylether of a polyethylene glycol of molecular weight 1500

A 60% strength ethyleneimine solution composed of 43 g (1 mol) of ethyleneimine and 29 g of ice is added dropwise to a catalyst solution composed of 3.0 g (0.05 mol) of ethylenediamine, 1.1 g (0.025 mol) of CO₂ and 17 g of deionized water at 90°C. The
30 mixture is then stirred at 90°C until the Preußmann test* for alkylating substances is negative. The product obtained in this way is crosslinked with the bisglycidyl ether by general method 1.

Example C

Amidation of polyethyleneimine with benzoic acid 20:1, crosslinked with bisglycidyl ether of a polyethylene glycol of molecular weight 1500

5

183.18 g of benzoic acid (1.5 mol) are introduced in portions into 1290 g of anhydrous polyethyleneimine (= 30 Eq N), prepared as in Example A, under nitrogen at 140°C. The mixture is then stirred at 180°C until the acid number is less than 5% of the initial value. The product obtained in this way is crosslinked with the bisglycidyl ether by
10 general method 1.

Example D

Amidation of polyethyleneimine with benzoic acid 10:1, crosslinked with bisglycidyl ether of a polyethylene glycol of molecular weight 1500

15

183.2 g of benzoic acid (1.5 mol) are introduced in portions into 645 g of anhydrous polyethyleneimine (= 15 Eq N), prepared as in Example B, under nitrogen at 140°C. The reaction temperature is raised to 180°C, and the water formed in the reaction is
20 distilled out under a gentle stream of nitrogen until the acid number is less than 5% of the initial value. The product obtained in this way is crosslinked with the bisglycidyl ether by general method 1.

General method 2

25

Crosslinking of tetraaminopropylethylenediamine and derivatives with bisglycidyl ether of a polyethylene glycol of molecular weight 1500

30

An approximately 20% strength aqueous solution of a polyethylene glycol bisglycidyl ether of molecular weight 1600 (or its bischlorohydrin) is added in portions to a 25% strength aqueous solution of tetraaminopropylethylenediamine at 70°C until the reaction solution has a viscosity of about 500 to 1000 mPas. If the pH falls below 9, NaOH (50% strength) is added in portions until the pH reaches 10.5.

This method can be used for tetraaminopropylethylenediamine, its higher homologs and for their amidation products with various degrees of amidation.

Example E

5

N,N,N',N'-Tetraaminopropyl-1,2-ethylenediamine (N6 amine), crosslinked with bisglycidyl ether of a polyethylene glycol of molecular weight 1500

Preparation of N,N,N',N'-tetracyanoethyl-1,2-ethylenediamine:

10

443 g (8.35 mol) of acrylonitrile are added over the course of 90 minutes to a solution of 100 g (1.67 mol) of 1,2-ethylenediamine in 1176 ml of water. The temperature must not exceed 40°C during this. After the addition of the acrylonitrile is complete, the flask is stirred for 1 hour at 40°C and for two further hours at 80°C. Excess acrylonitrile is subsequently distilled off, and then most of the water is distilled off by applying a water pump or oil pump vacuum. The tetracyanoethylated ethylenediamine is recrystallized from methanol and filtered off with suction. The yield is 478 g (1.58 mol).

15

Preparation of N,N,N',N'-tetraaminopropyl-1,2-ethylenediamine N6 amine):

20

400 ml/h of a mixture of 20% by weight N,N,N',N'-tetracyanoethyl-1,2-ethylenediamine and 80% by weight N-methylpyrrolidone and 3500 ml/h of ammonia are passed over 4 l of a fixed bed catalyst of composition 90% by weight CoO, 5% by weight MnO, 5% by weight P₂O₅ in a 5 l fixed bed reactor at 130°C under a pressure of 200 bar of hydrogen. Removal of the N-methylpyrrolidone under reduced pressure and fractional distillation (boiling point: 218°C under 6 mbar) result in N,N,N',N'-tetraaminopropyl-1,2-ethylenediamine (N6 amine) in 95% yield. The product was checked for purity and completeness of the reaction by ¹³C and ¹H NMR and mass spectroscopy.

25

30

The product obtained in this way is crosslinked with the bisglycidyl ether by general method 2.

(* Preußmann test = test for alkylating compounds, procedure described by J. Epstein et al., *Analyt. Chem.* 27 (1955) 1435 and R. Preußmann et al., *Arzneimittelforsch.* 19 (1969) 1059.)

5 Washing tests

The soil release effect of the compounds according to the invention was determined in washing tests in a Launder-O-meter under standardized conditions. The detergent formulation (composition I in Table 4) was used for the tests. Use of detergent
10 formulations II to XI is likewise possible according to the invention.

Detergent formulation I was initially investigated without a compound according to the invention and subsequently with the compounds according to the invention from Examples A to E in concentrations of 2% of the total weight of detergent. The test
15 fabrics were prewashed three times with detergent formulation I with these additives (prewash; washing conditions hereinafter), dried and stained with 0.2 g of used engine oil. The oil spots were left to age for 14 hours. The test fabrics were then washed again with detergent formulation I with additives (main wash), and the soil detachment was
determined.

20

Washing conditions

Machine:	Launder-O-meter from Atlas, Chicago
Wash liquor:	250 ml
25 Washing time:	30 min at 60°C
Detergent dose:	6 g/l
Water hardness:	3 mmol; Ca: Mg 4:1
Liquor ratio:	1:12.5
Test fabrics:	Cotton 221, PES850, PES/cotton 65:35 blended fabric

30

Washing result

To determine the washing result, the reflectances were determined for the test fabric

before washing (R_0), for the stained test fabric before the main wash (R before) and after the main wash (R after). The percentage soil release was then determined using

$$\% \text{ soil release} = (R \text{ after} - R \text{ before}) / (R_0 - R \text{ before}) \times 100$$

5

A higher percentage soil release means better removal of the spot. Complete removal of the spot corresponds to 100%. The crucial point in this connection is the difference in % soil release between the detergent formulation without and with the compound according to the invention. A greater difference between % soil release without and with compound according to the invention means a greater improvement in the washing result with the detergent formulation on addition of the compound according to the invention. The results of the washing tests are indicated in Tables 1 and 2.

10

Table 1

15

**Improvement in the soil detachment by addition of
2% of the compounds according to the invention**

Fabric: Polyester PES 850

Example	R before	R after	Difference	% Soil release
without	23.6	50.5	26.9	45.3
A	24.1	64.4	40.3	68.5
B	25.4	65.8	40.4	70.3
C	24.7	96.2	44.5	76.4
D	24.6	67.7	43.1	73.8
E	25.1	64.5	39.4	68.2

20

Table 2
Difference between single wash cycle performance
and soil release effect

5 *Fabric: Polyester PES 850*

Example	Mode	R before	R after	% Soil Release	% SR with - % SR without*
A	with/without	22.4	55	53.8	13.2
	without/with	23.8	44.5	34.9	-5.7
D	with/without	23.7	63.7	67.4	26.8
	without/with	23.8	46.4	38.2	-2.4
E	with/without	23.9	60.2	61.4	20.8
	without/with	23.8	47.2	39.5	-1.1

*: % SR without = 40.6

10 It is evident from Tables 1 and 2 that the compounds according to the invention of Examples A to E distinctly improve soil detachment during washing. The degree of whiteness of the fabric after washing, R after, is significantly improved by adding the compounds according to the invention.

15 The results indicated in Table 2 make it clear that the improved soil detachment is a soil release effect and not a pure single wash cycle effect. In the series of tests on which this test was based, two different application variants were carried out:

Mode 1: three prewashes with detergent with additive, main wash (after staining) without additive in the detergent (= with/without)

20

Mode 2: three prewashes without additive in the detergent, main wash (after staining) with detergent with additive (= without/with)

If, in Mode 1, there is an improvement in soil detachment compared with the test with prewash and main wash with detergent but without additive (% SR without), a soil release effect is achieved. If, in Mode 2, there is an improved soil detachment, a single wash cycle effect is achieved. It is evident from the results in Table 2 that improved soil detachment can be achieved only in Mode 1, so that the effect achieved by the products according to the invention derives from a soil release action.

The crosslinked polyamines were also employed in combination with corresponding but uncrosslinked polyamines. The results are shown in Table 3.

Table 3

**Improvement in soil detachment on addition of combinations of
uncrosslinked and crosslinked polyamines**

In each case 2 + 2% test substance

Example	Cotton			Blended fabric			Polyester		
	R before	R after	% SR	R before	R after	% SR	R before	R after	% SR
without	22.7	63	69.4	25.4	60.1	60.3	19.2	41.9	35.9
A + A'	21.6	65.9	74.4	21.9	64.5	96.8	16.4	55.2	58.9
C + C'	21.8	67.8	77.9	24.8	70.9	79.3	18.3	62	68.4
E + E'	21.7	68.3	78.7	24.3	70.8	79.3	19.3	56.3	59.2
C + OA	21.9	77.3	94	21.7	71.2	80.8	19.4	74	86.9

A' = Example A, uncrosslinked

C' = Example C, uncrosslinked

E' = Example E, uncrosslinked

OA = octylamine

It is evident from the results shown in Table 3 that mixtures of crosslinked and uncrosslinked polyamines can be employed advantageously for washing all common textiles such as cotton, polyester and fabrics blended from cotton and polyester.

Ingredients	Composition in %											
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Mg silicate	1	1	2	2	2	3	3					
Na silicate			2	2	2	3	3					
Zeolite A	45	45	40	40	40	36	20	30	30	30	30	20
Zeolite P							10					
Sheet silicate SKS6												15
Sodium carbonate	7	7	6	6	6	12	10	8	8	8	8	
Sodium citrate	12	12				5						5
Sodium citrate x 2H ₂ O			18	18	18							
MGDA tri-Na							5	5	5			
Phosphonate				1						1	2	
TAED						4	4	4	4	4	4	5
Sodium perborate x 4H ₂ O									20			
Sodium perborate x 1H ₂ O								14.4		14.4	14.4	
Sodium percarbonate						15	15					15
Carboxymethylcellulose	1	1	1	1	1	1.5	1	1.2	1.2	1.2	1.2	1
Lipase	0.2	0.2			0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Protease	0.3	0.3			0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Cellulase	0.5	0.5			0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sodium sulfate	3	3	3	3	3	2	3	3	3	3	3	3

Enzyme-stabilizing action

To test the enzyme-stabilizing action of the compounds according to the invention, they were incorporated into a liquid detergent formulation, and a protease was added to the latter. After 25 and 50 days, washing tests were carried out with soiled test fabric. Detergent formulations without added enzyme and with added enzyme but without addition of the compounds according to the invention were used for comparison.

The washing tests were evaluated by measuring the color strength of the test fabrics and determining the single wash cycle effect A_{abs} from the color strength by the method described in A. Kud, Seifen, Öle, Fette, Wachse, 119 (1993), 590-594.

Test conditions

Storage:

Storage temperature for the liquid detergent formulation: 30°C

Enzyme: Protease, Savinase® 16L (manufactured by Novo Nordisk)

Amount of enzyme: 0.4% Savinase 16L

Storage time: 50 days

Washing conditions:

Machine: Launder-O-meter

Soiled fabric: 2.5 g of CFT AS 10 (Pigment/oil/milk)

Ballast fabric: 5.0 g of cotton

Detergent: Formulation XII hereinafter

Amount: 4.0 g/l

Amount of liquor: 250 g

Washing temperature: 20°C

Water hardness: 3 mmol/l
Ca/Mg ratio: 4.0 : 1.0
Washing time: 15 min

5 *Detergent formulation XII:*

	Linear alkylbenzenesulfonate	19.5	
	Coconut fatty acid	8.3	
	C _{13/15} oxo alcohol ethoxylate	16.8	
10	Ethanol	0.7	
	1,2-Propanediol	11.0	
	Ethanolamine	9.4	
	Citric acid	4.8	
	Sokolan®CP5	0.9	
15	Dequest® 2006	1.0	
	(manufactured by Monsanto) Savinase® 16L	0.4 (or 0 in the comparative test without enzyme)	
	Polymer according to the invention		
20		2.5 (or 0 in the comparative test without polymer)	

The results are listed in Table 5 hereinafter.

Table 5

Results of tests on enzyme stabilization

Test	Storage [days]	Amount of enzyme [%]	Polymer	Amount of polymer [%]	Single wash cycle effect A_{500} [%]
1	25	-	-	-	38
2	25	0.4	-	-	55
3	25	-	C	2.5	37
4	25	0.4	C	2.5	66
5	50	-	-	-	41
6	50	0.4	-	-	46
7	50	0.4	C	2.5	68

5

The polymer from Example C was used as polymer. The results in Table 5 show that a distinctly improved enzyme activity on prolonged storage is achieved with the crosslinked compounds according to the invention by comparison with the tests without added polymer. After storage of the liquid detergent without compound according to the invention at 30°C for 50 days, the protease action has been almost completely lost, whereas there is still a high protease activity in the formulations with compound C after 50 days.

10

We claim:

1. The use of crosslinked nitrogenous compounds which are soluble or dispersible in water and are obtainable by crosslinking of
 - (a) compounds containing at least three NH groups with
 - (b) at least bifunctional crosslinkers which react with NH groups, in detergents and cleaners.
2. The use as claimed in claim 1, wherein compounds (a) are selected from the group consisting of oligo- and polyamines, polyalkylenepolyamines, polyamidoamines, polyamidoamines grafted with (poly)ethyleneimine, and mixtures thereof.
3. The use as claimed in claim 1 or 2, wherein the crosslinkers (b) are selected from the group consisting of the halogen-free crosslinkers
 - (1) polyepoxides
 - (2) ethylene carbonate, propylene carbonate and/or urea,
 - (3) monoethylenically unsaturated carboxylic acids and their esters, amides and anhydrides, at least dibasic carboxylic acids or polycarboxylic acids, and their esters, amides and anhydrides,
 - (4) products of the reaction of polyetherdiamines, alkylenediamines, polyalkylenepolyamines, bifunctional or multifunctional alcohols, alkylene glycols, polyalkylene glycols, functionalized polyesters or polyamides or their mixtures with monoethylenically unsaturated carboxylic acids or their esters, amides or anhydrides, the reaction products having at least two ethylenic double bonds, carboxamide, carboxyl or ester groups as functional groups,
 - (5) products, containing at least two aziridino groups, of the reaction of dicarboxylic esters with ethyleneimine,
 - (6) cumulenes and polyheterocumulenes,

- (7) β -keto esters, β -keto acids and β -keto aldehydes,
(8) functionalized glycidyl ethers,
the halogen-containing crosslinkers
(9) polyhalides
5 (10) glycidyl halides,
(11) chloroformates and chloroacetic acid derivatives,
(12) epichlorohydrin, glycerol chlorohydrin, polyether dichlorohydrin
compounds,
(13) phosgene
10 or mixtures thereof.

4. The use as claimed in any of the preceding claims, wherein compound (a) is
selected from N,N,N',N'-tetraaminopropyl-1,2-ethylenediamine or polyethylene-
imine with a degree of polymerization of from 5 to 50, and crosslinker (b) is a
15 bisglycidyl ether of a polyethylene glycol with a weight average molecular
weight of from 300 to 3000.

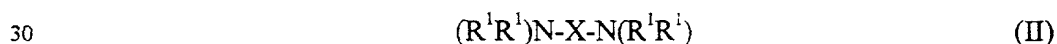
5. The use as claimed in any of the preceding claims as soil release agents.

20 6. The use as claimed in any of claims 1 to 4 as enzyme stabilizers.

7. A detergent or cleaner comprising at least one crosslinked nitrogenous
compound as defined in any of claims 1 to 4, and at least one surfactant.

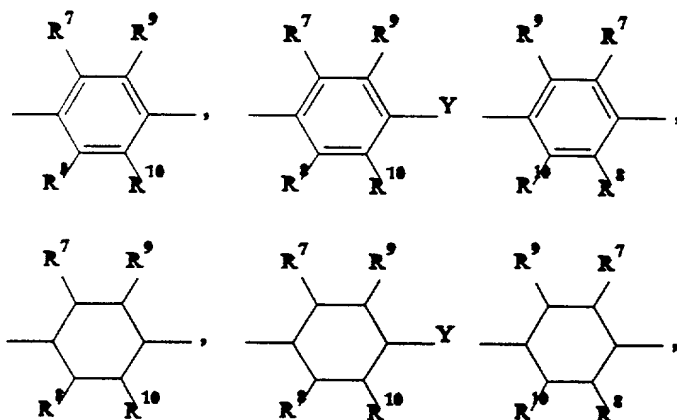
25 8. A detergent or cleaner as claimed in claim 7, additionally comprising at least one
enzyme.

9. A water-soluble crosslinked product obtainable by crosslinking amines of the
formula (II)



where the radicals R^1 are hydrogen atoms or $(R^2R^2)N-(CH_2)_n-$ radicals,
the radicals R^2 are hydrogen atoms or $(R^3R^3)N-(CH_2)_n$ radicals,
the radicals R^3 are hydrogen atoms or $(R^4R^4)N-(CH_2)_n-$ radicals,
the radicals R^4 are hydrogen atoms or $(R^5R^5)N-(CH_2)_n-$ radicals,
5 the radicals R^5 are hydrogen atoms or $(R^6R^6)N-(CH_2)_n-$ radicals,
the radicals R^6 are hydrogen atoms,
n is 2, 3 or 4, and
the radical X is one of the radicals

10



$-(CH_2)_p-$, $-(CH_2)_3-NR^{11}-(CH_2)_3-$, $-(CH_2)_1-[O-(CH_2)_k]_m-O-(CH_2)_1-C_{2-20}$ -alkylene,

the radical Y is an oxygen atom, a $CR^7R^9C=O$ or SO_2 radical,

p is an integer from 2-20,

l and k are, independently of one another, an integer from 2-6, m is an integer
5 from 1-40,

the radicals R^7 , R^8 , R^9 and R^{10} are, independently of one another, hydrogen
atoms or C_{1-6} -alkyl radicals,

and the radical R^{11} is C_{1-20} -alkyl, C_{2-20} -dialkylamino- C_{2-10} -alkyl, C_{1-10} -alkoxy- C_{2-10} -alkyl, C_{2-20} -hydroxyalkyl, C_{3-12} -cycloalkyl, C_{4-20} -cycloalkylalkyl, C_{2-20} -alkenyl,
10 C_{4-30} -dialkylaminoalkenyl, C_{3-30} -alkoxyalkenyl, C_{3-20} -hydroxyalkenyl, C_{5-20} -
cycloalkylalkenyl, an aryl or a C_{7-20} -arylalkyl radical which is unsubstituted or
substituted one to five times by C_{1-8} -alkyl, C_{2-8} -dialkylamino, C_{1-8} -alkoxy,
hydroxyl, C_{3-8} -cycloalkyl and/or C_{4-12} -cycloalkylalkyl, or two radicals R^{11}
together form an alkylene chain which may be interrupted by nitrogen or
15 oxygen, such as from ethylene oxide, propylene oxide, butylene oxide and $-CH_2-$
 $CH(CH_3)-O-$ or polyisobutylene with 1 to 100 isobutylene units,

with at least one crosslinker (b) as defined in claim 1, 3 or 4.

- 20 10. The use of a detergent or cleaner as claimed in either of claims 7 or 8 for
washing textiles.

Abstract

The invention relates to the use of crosslinked nitrogenous compounds which are soluble or dispersible in water and are obtainable by crosslinking of

5

- (a) compounds containing at least three NH groups with
- (b) at least bifunctional crosslinkers which react with NH groups,

10 in detergents and cleaners, especially soil release agents.

Compounds (a) are preferably selected from the group consisting of oligo- and polyamines, polyalkylenepolyamines, polyamidoamines, polyamidoamines grafted with (poly)ethyleneimine, and mixtures thereof.

15

THE FOLLOWING IS THE ENGLISH TRANSLATION OF THE ANNEXES TO THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT: (pages 46-49)

as enclosed to IPER

We claim:

- 5 1. The use of crosslinked nitrogenous compounds which are soluble or dispersible in water and are obtainable by crosslinking of
 - (a) compounds containing at least three NH groups with
 - (b) at least bifunctional crosslinkers which react with NH groups,
 in detergents and cleaners as soil release agents and/or enzyme stabilizers.
- 10 2. The use as claimed in claim 1, wherein compounds (a) are selected from the group consisting of oligo- and polyamines, polyalkylenepolyamines, polyamidoamines, polyamidoamines grafted with (poly)ethyleneimine, and mixtures thereof.
- 15 3. The use as claimed in claim 1 or 2, wherein the crosslinkers (b) are selected from the group consisting of the halogen-free crosslinkers
 - (1) polyepoxides
 - (2) ethylene carbonate, propylene carbonate and/or urea,
 - 20 (3) monoethylenically unsaturated carboxylic acids and their esters, amides and anhydrides, at least dibasic carboxylic acids or polycarboxylic acids, and their esters, amides and anhydrides,
 - (4) products of the reaction of polyetherdiamines, alkylenediamines, polyalkylenepolyamines, bifunctional or multifunctional alcohols, alkylene glycols, polyalkylene glycols, functionalized polyesters or polyamides or their mixtures with
 - 25 monoethylenically unsaturated carboxylic acids or their esters, amides or anhydrides, the reaction products having at least two ethylenic double bonds, carboxamide, carboxyl or ester groups as functional groups,
 - (5) products, containing at least two aziridino groups, of the reaction of dicarboxylic esters with ethyleneimine,
- 30

- (6) cumulenes and polyheterocumulenes,
 (7) β -keto esters, β -keto acids and β -keto aldehydes,
 (8) functionalized glycidyl ethers,
 the halogen-containing crosslinkers
 (9) polyhalides
 (10) glycidyl halides,
 (11) chloroformates and chloroacetic acid derivatives,
 (12) epichlorohydrin, glycerol chlorohydrin, polyether dichlorohydrin compounds,
 (13) phosgene
 or mixtures thereof.

4. The use as claimed in any of the preceding claims, wherein compound (a) is selected from amines of the general formula (II) according to claim 8 or polyethyleneimine with a degree of polymerization of from 5 to 50, and crosslinker (b) is a bisglycidyl ether of a polyethylene glycol with a weight average molecular weight of from 300 to 3000.

5. The use as claimed in claim 4, wherein the compound (a) is N,N,N',N'-tetraaminopropyl-1,2-ethylenediamine.

6. A detergent or cleaner comprising at least one crosslinked nitrogenous compound as defined in any of claims 4 or 5, and at least one surfactant.

7. A detergent or cleaner as claimed in claim 6, additionally comprising at least one enzyme.

8. A water-soluble crosslinked product obtainable by crosslinking amines of the formula (II)



where the radicals R^1 are $(R^2R^2)N-(CH_2)_n$ - radicals,

the radicals R^2 are hydrogen atoms or $(R^3R^3)N-(CH_2)_n$ radicals,

the radicals R^3 are hydrogen atoms or $(R^4R^4)N-(CH_2)_n$ radicals,

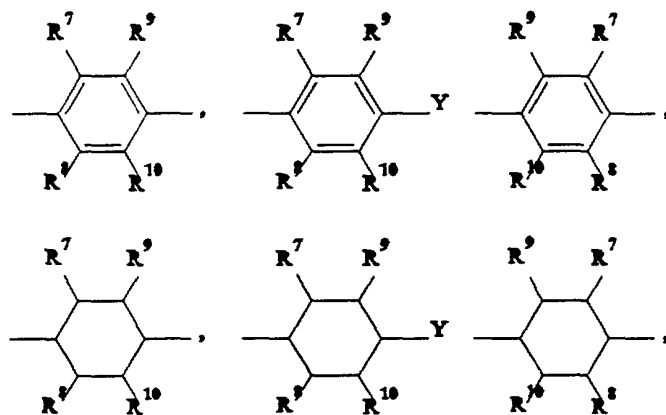
the radicals R^4 are hydrogen atoms or $(R^5R^5)N-(CH_2)_n$ radicals,

5 the radicals R^5 are hydrogen atoms or $(R^6R^6)N-(CH_2)_n$ radicals,

the radicals R^6 are hydrogen atoms,

n is 2, 3 or 4, and

the radical X is one of the radicals



$-(CH_2)_p-$, $-(CH_2)_3-NR^{11}-(CH_2)_3-$, $-(CH_2)_1-[O-(CH_2)_k]_m-O-(CH_2)_1-C_{2-20}$ -alkylene,

the radical Y is an oxygen atom, a $CR^7R^9C=O$ or SO_2 radical,

p is an integer from 2-20,

l and k are, independently of one another, an integer from 2-6, m is an integer from 1-40,

the radicals R^7 , R^8 , R^9 and R^{10} are, independently of one another, hydrogen atoms or C_{1-6} -alkyl radicals,

and the radical R^{11} is C_{1-20} -alkyl, C_{2-20} -dialkylamino- C_{2-10} -alkyl, C_{1-10} -alkoxy- C_{2-10} -alkyl, C_{2-20} -hydroxyalkyl, C_{3-12} -cycloalkyl, C_{4-20} -cycloalkylalkyl, C_{2-20} -alkenyl, C_{4-30} -dialkylaminoalkenyl, C_{3-30} -alkoxyalkenyl, C_{3-20} -hydroxyalkenyl, C_{5-20} -cycloalkylalkenyl, an aryl or a C_{7-20} -arylalkyl radical which is unsubstituted or substituted one to five times by C_{1-8} -alkyl, C_{2-8} -dialkylamino, C_{1-8} -alkoxy, hydroxyl, C_{3-8} -cycloalkyl and/or C_{4-12} -cycloalkylalkyl, or two radicals R^{11} together form an alkylene chain which may be interrupted by nitrogen or oxygen, such as from ethylene oxide, propylene oxide, butylene oxide and $-CH_2-CH(CH_3)-O-$ or polyisobutylene with 1 to 100 isobutylene units,

with at least one crosslinker (b) as defined in claim 1, 3 or 4.

9. A water-soluble crosslinked product of claim 8, in which the amine of general formula (II) is N,N,N',N'-tetraaminopropyl-1,2-ethylene diamine.

Declaration, Power of Attorney

Page 1 of 4

O. Z. 0050/47419

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name.

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

✓ The use of crosslinked nitrogenous compounds which are soluble or dispersible in water in detergents and cleaners

the specification of which

☐ is attached hereto.

☐ was filed on _____ as

Application Serial No. _____

and amended on _____.

☒ was filed as PCT international application

✓ Number PCT/EP97/05744

✓ on October 17, 1997

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)–(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19643133.6	Federal Republic of Germany	18th October 1996	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No

O. Z. 0050/47419

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

 (Application Number)

 (Filing Date)

 (Application Number)

 (Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.

Filing Date

Status (pending, patented,
abandoned)

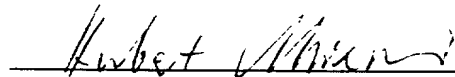
And we (I) hereby appoint: Norman F. Oblon, Registration Number 24, 618;
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 Timothy R. Schwartz, Registration Number 32, 171;
 Stephen G. Baxter, Registration Number 32, 884;
 Richard L. Treanor, Registration Number 36, 379;
 Robert W. Hahl, Registration Number 33, 893, our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of **OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P. C.**, whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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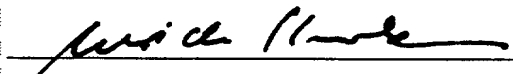
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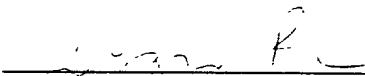
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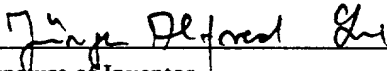
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